Detailing new and emerging groundwater pollutants and their potential risk to groundwater environments

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Groundwater 2014
Regulatory Updates & Practical Solutions for Improved Risk Assessment, Quality & Resource Protection

Emerging organic contaminants

www.gardenorganic.co.uk

- Anthropogenic organic compounds and their transformation products
- Emerge as result of:
  - Changes in use of manufactured chemicals
  - Advances in analytical techniques
  - Better monitoring
- Most do not have quality standards
- Generally ECs in groundwater less well characterised than surface water, mainly due to lower concentrations

Emerging (ed) organic contaminants

- Pesticides – parent compounds (e.g. metaldehyde), metabolites
- Pharmaceuticals – human, veterinary, illicit
- “Life style” – nicotine, caffeine, sweeteners
- Personal care – DEET, parabens, triclosan, musks, UV filters
- Industrial additives and by-products – dioxanes, bisphenols, MTBE
- Food additives – BHA, BHT
- Water and wastewater treatment by-products – NDMA, THM
- Flame/fire retardants – PBDE, alkyl phosphates, triazoles
- Surfactants – alkyl ethoxylates, PFOS & PFOA
- Hormones and sterols – estradiol, cholesterol

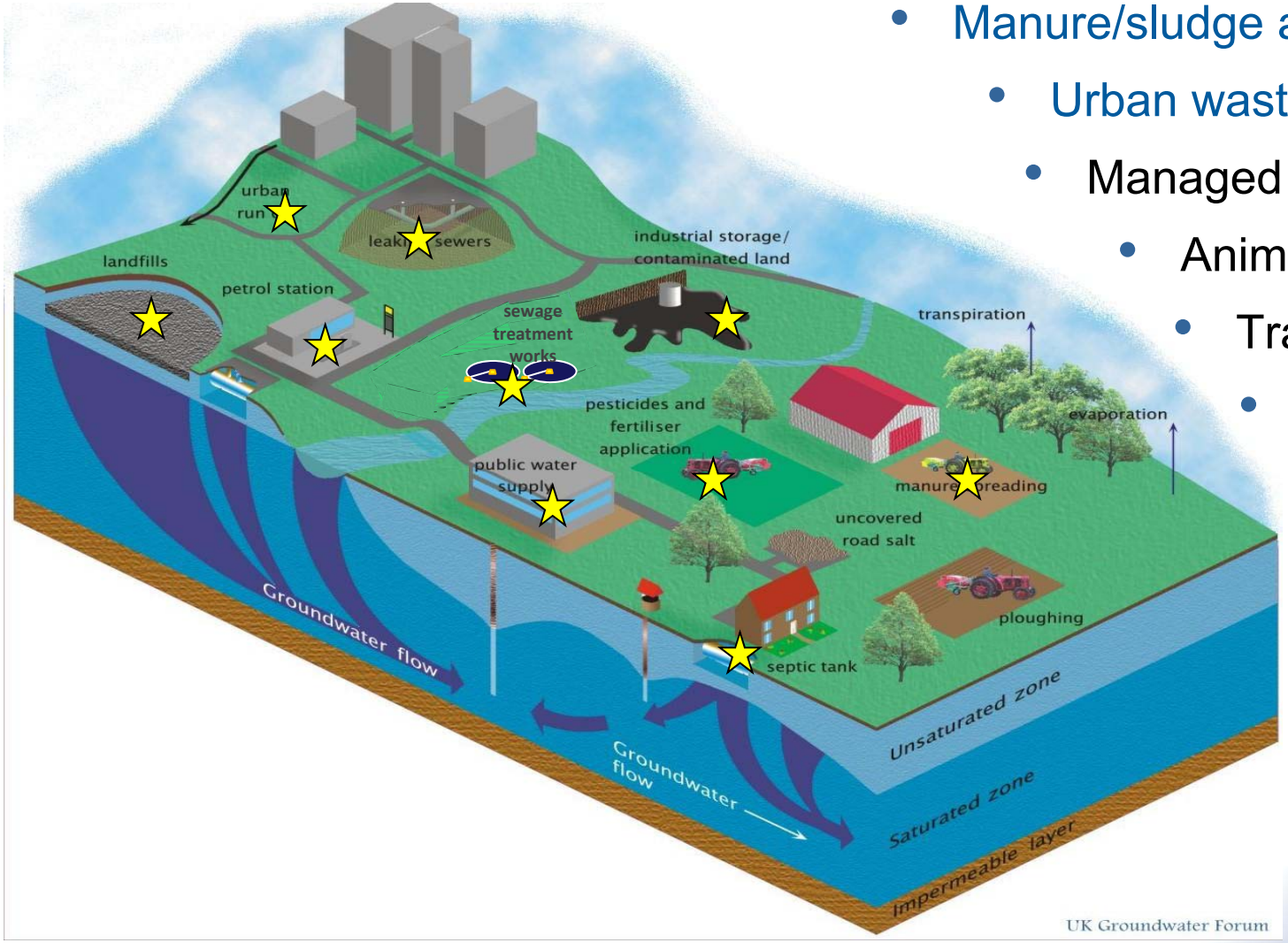
Transformation products

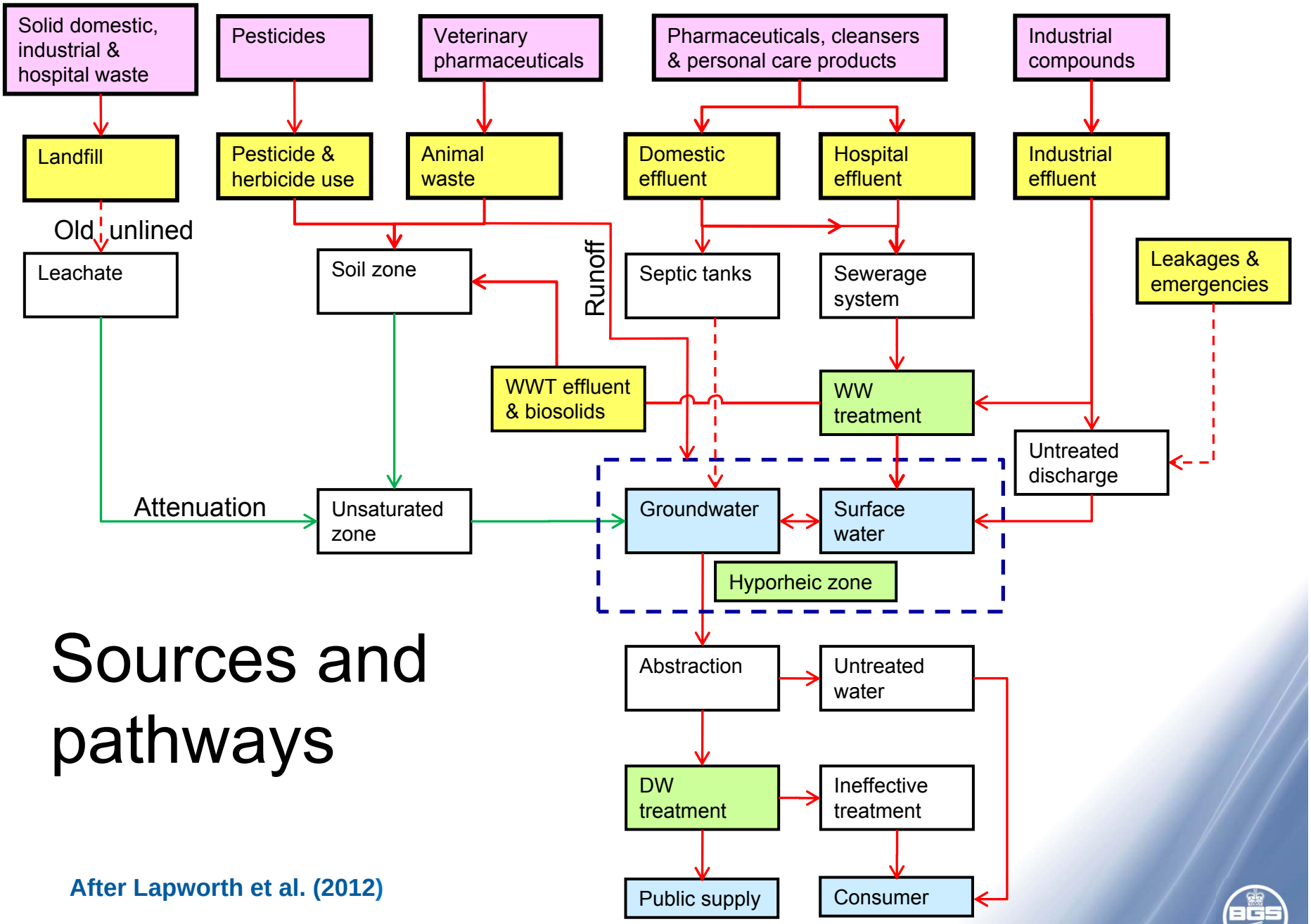
- May be more toxic, polar or persistent than the parent
- For pesticides:
  - Desethyl, desisopropyl - atrazine
  - BAM from diclobenil
  - AMPA from glyphosate
- Common EC TPs>parent concentrations have been:
  - Cotinine from nicotine
  - Clofibric acid from clofibrate
  - Nonyl phenol from NPE
- Cannot be reliably predicted from surface environments data due to different geochemical conditions and long residence times
- May have long arrival time due to thick unsaturated zone or low aquifer permeability

Stuart & Lapworth (2014)

Sources of ECs in groundwater

- Treated wastewater discharge to surface water
- Manure/sludge application to soil
- Urban waste water drainage
- Managed aquifer recharge
- Animal waste lagoons
- Transport networks
- Water treatment
- Septic tanks
- Landfill





Sources and pathways

After Lapworth et al. (2012)

New Priority Substances

- 2012 Commission proposal on priority substances (COM(2011)876)
- New priority substances - aclonifen, bifenox, cybutryne, cypermethrin isomers, dichlorvos, dicofol, dioxins*, hexabromocyclododecane*, heptachlor/ heptachlor epoxide*, PFOS*, quinoxyfen*, terbutryne

  *designated as priority hazardous substances
- Supplementary monitoring programmes for new substances to be in place by 2018
- Revised EQS for existing substances – including anthracene, fluoranthene, naphthalene, PBDEs, trifluralin to be included in RBMPs by 2015
- For surface water but also impact of groundwater

Watch lists

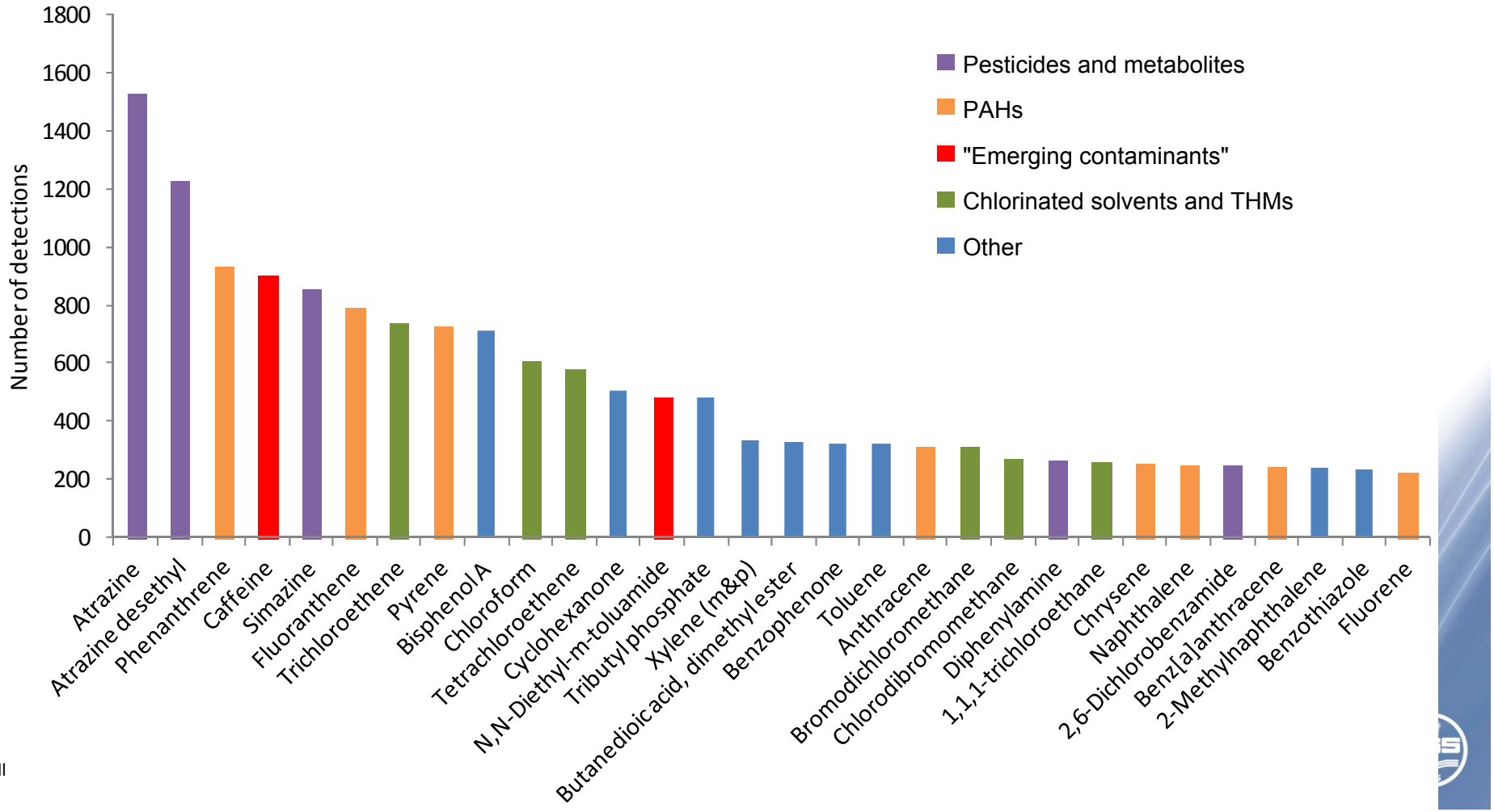
Surface water

- Priority Substances Directive amendment 2013/39/EU
- Targeted EU-wide monitoring of substances of possible concern to support the prioritisation process in future reviews (10-14 in rolling programme)
- First watch list -17α-ethinylestradiol,17β-estradiol, diclofenac

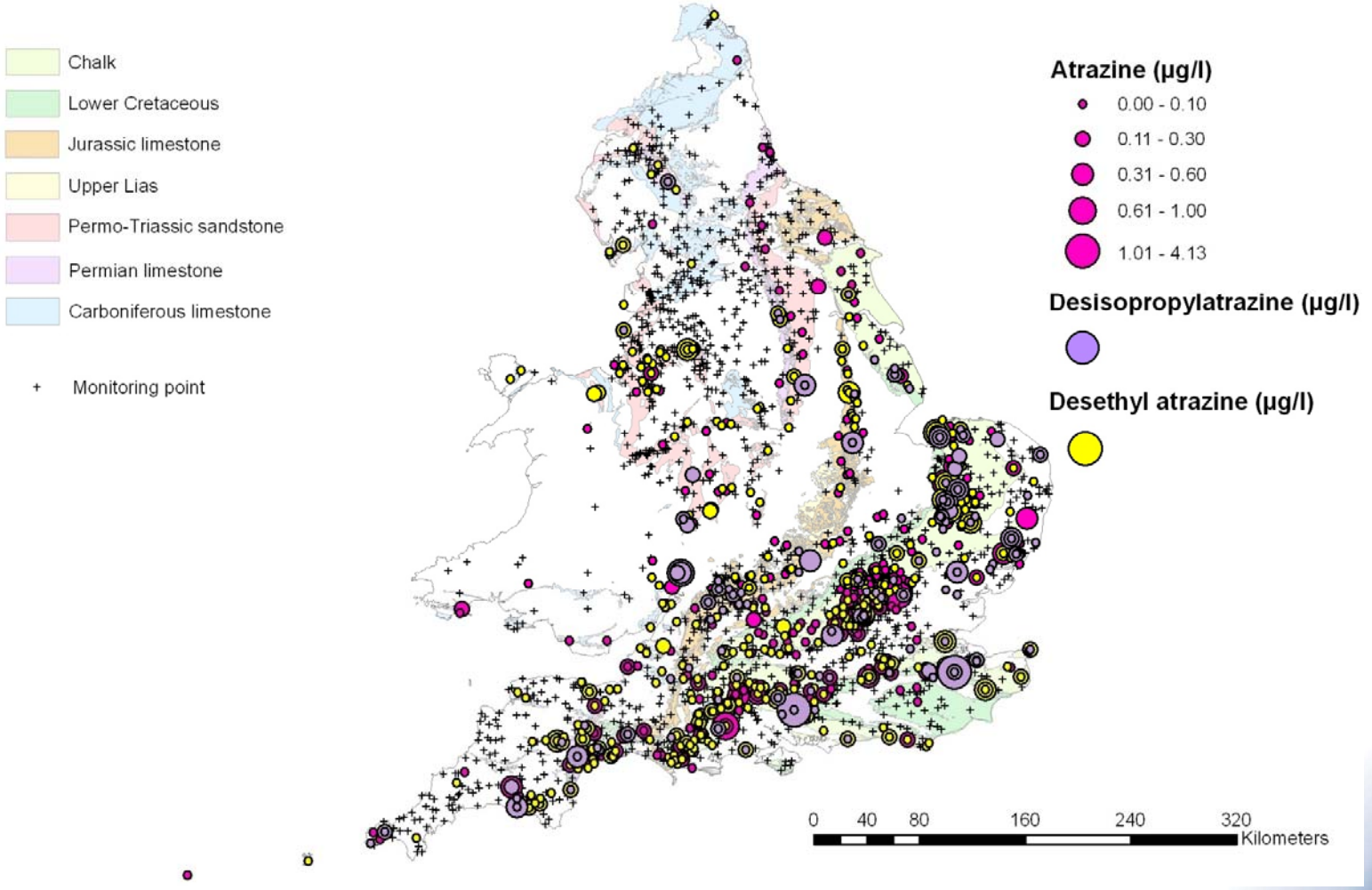
Groundwater

- Draft COM Directive (Recital 4) amending Annex II of the GWD
- Less developed than surface water
- Increased availability of monitoring data to facilitate identification of substances

Top 30 microorganics in Environment Agency groundwater screening data 1993-2012



Atrazine and its metabolites in groundwater



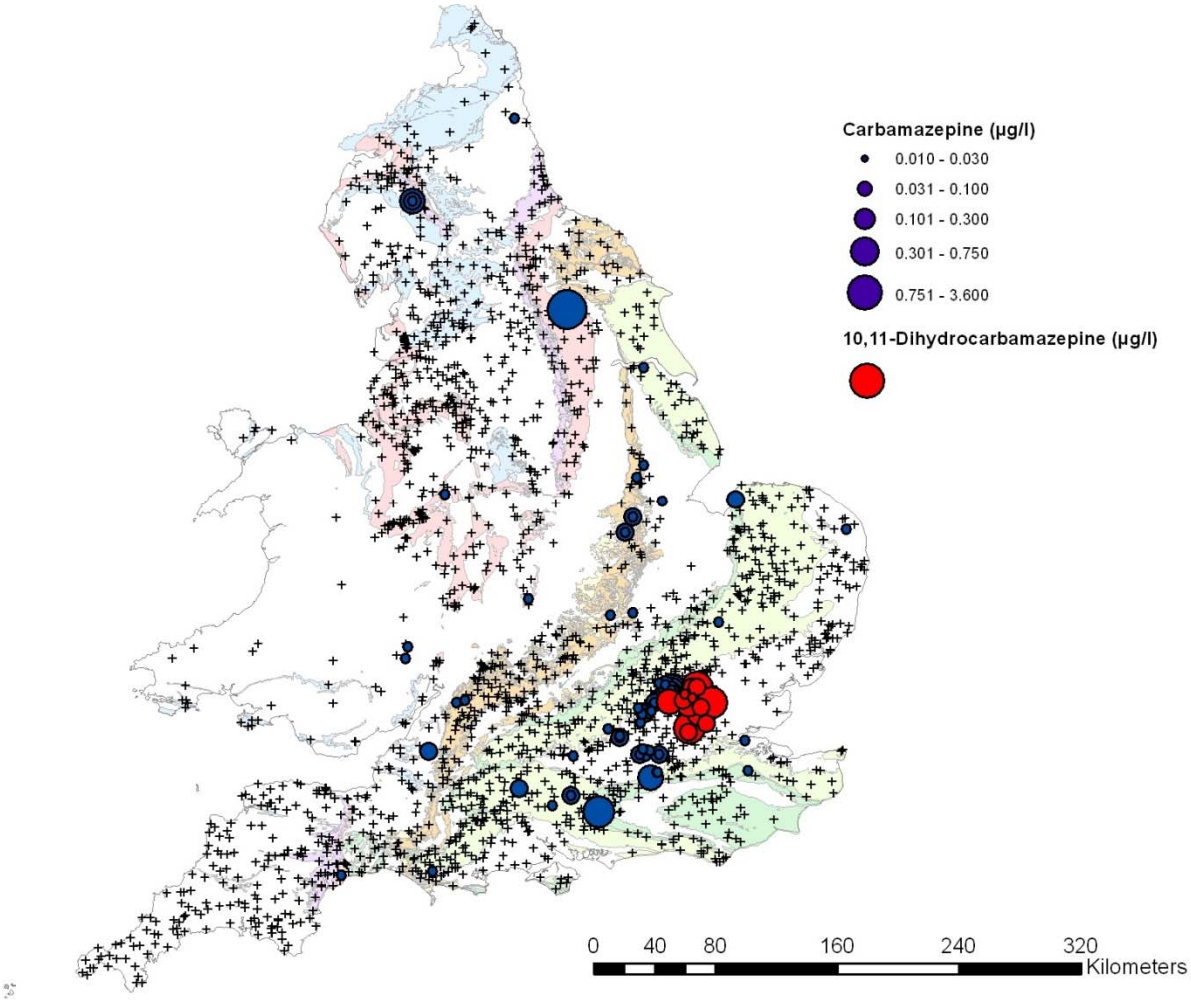
Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

Pharmaceuticals

- Next most frequently reported group after pesticides
- Most common are:
  - Analgesics (paracetamol>ibuprofen>phenazone>propyphenazone >salicylic acid)
  - Anti-inflammatories (ibuprofen>ketoprofen>diclofenac)
  - Antibiotics (sulfamethoxazole>lincomycin>erythromycin)
  - Anti-epileptics (carbamazepine)
  - Barbiturates (primidone)
  - Lipid regulators (fenofibrate, clofibrate)
  - Insecticides (DEET)
  - X-ray contrasting agents (iopamidol)
  - Veterinary medicines (sulfamethazine, monensin, tylosin)

Lapworth et al. (2012); Barnes et al. (2004, 2008); Watanabe et al. (2010); Scheytt et al (2007); López-Serna (2013)

Carbamazepine in groundwater



- Used to treat epilepsy and bipolar disorder
- Possible biotransformation product

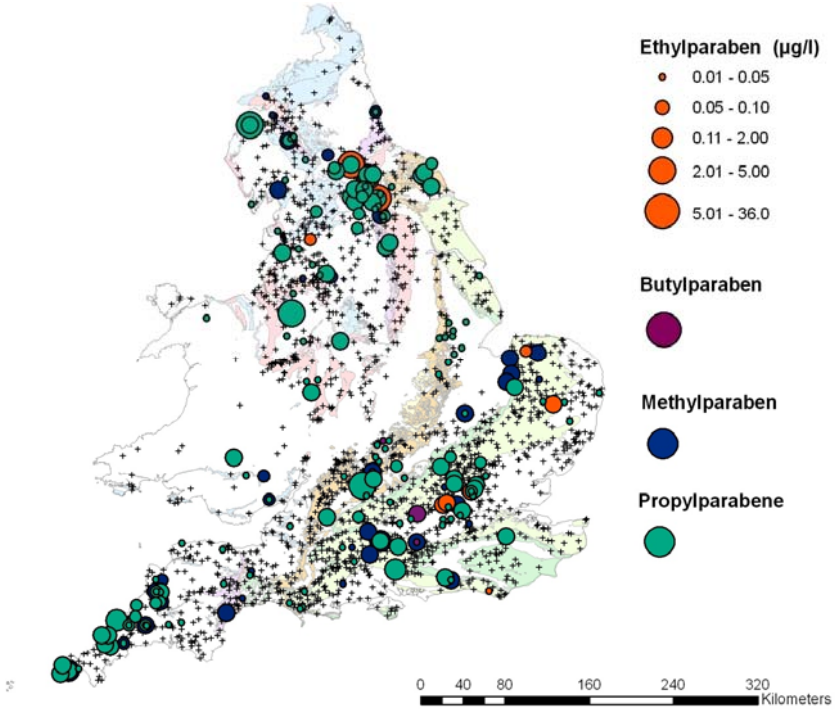
Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

Personal care products

- Skin care products:
  - UV blockers, isopropyl myristate, phenoxy-ethanol, lilial
- Anti-bacterial agents
  - Parabens and triclosan
- Polycyclic musks
  - Galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI) and phantolide (AHDI), and the nitro musks (musk xylene and musk ketone)
  - Musks are degraded to more polar compounds in water treatment and in the soil
  - HHCB-lactone, 2-amino-musk ketone, 4-amino musk ketone, 2-amino-musk xylene in effluents

Martin et al. (2007), Matamoros et al, (2009)

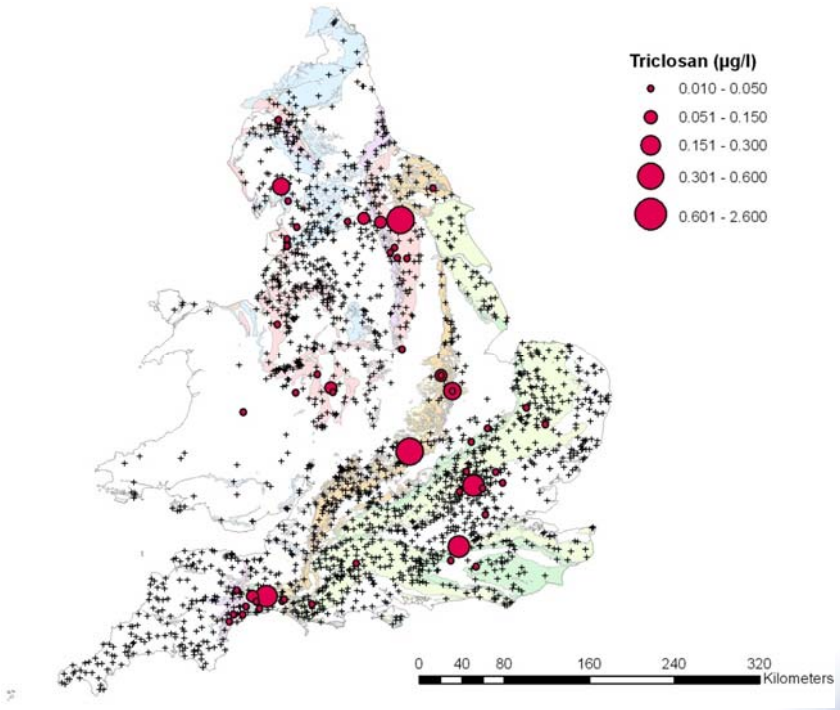
Bactericidal and fungicidal PCPs in groundwater



Parabens

- Widely used
- Potential links with cancer and endocrine disruption

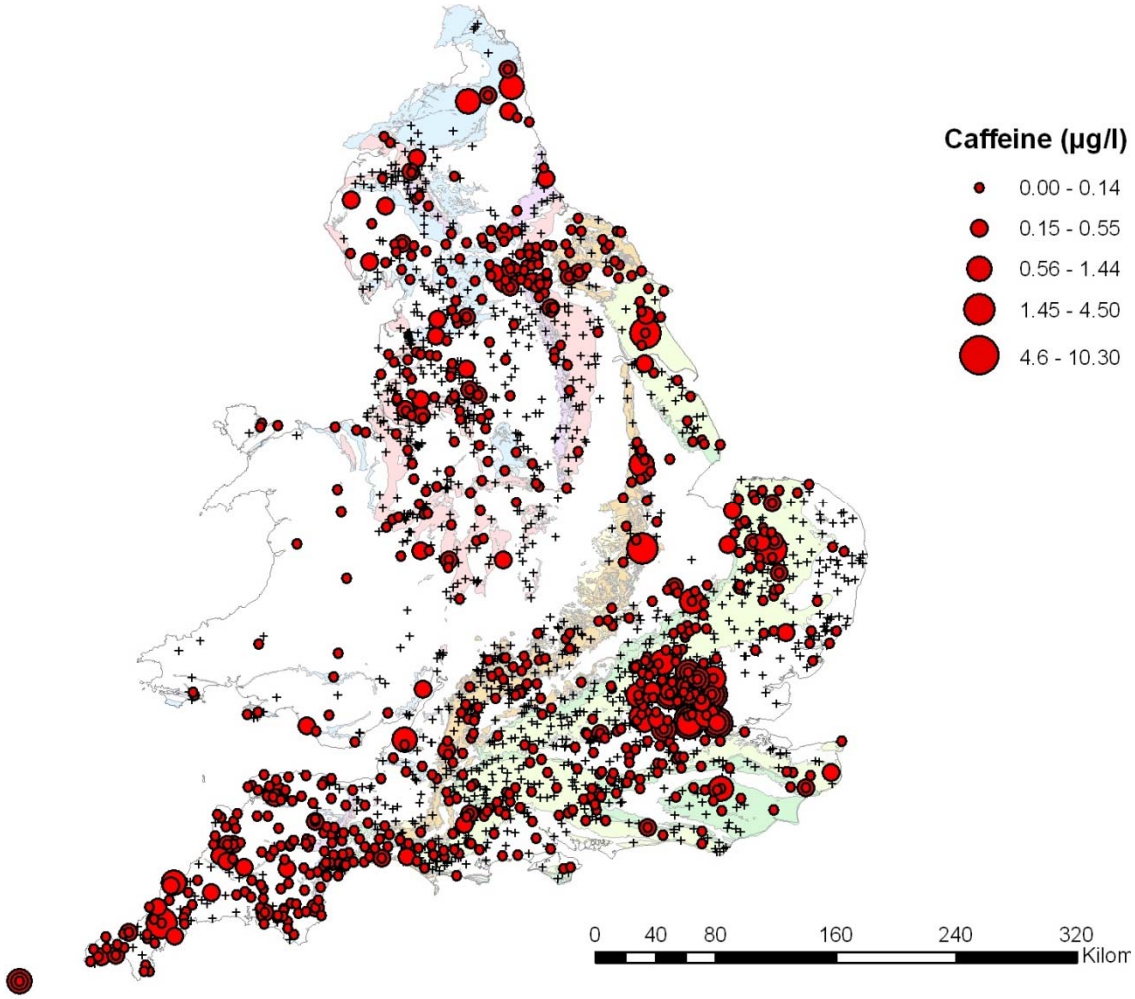
Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning



Triclosan

- Used since 1972 especially for hands
- Bacterial resistance concerns
- Reacts with chlorine to dioxin precursor

Caffeine and nicotine



- Caffeine, nicotine and cotinine (nicotine metabolite), from sewage effluent, are widely detected in groundwater
- Paraxanthine (caffeine metabolite) also found
- Dimethyl-imidazo-lidinetrione (product of caffeine chlorination) also found elsewhere

Barnes et al. (2008);
Seiler et al. (1999);
Swartz et al. (2006)

Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

Brominated and fluorinated compounds

PBDE & PDB

- Flame retardants - polybrominated diphenyl ether and polybrominated biphenyl cogeners.
  - Concern that the lower de-brominated PBDEs more toxic than parent

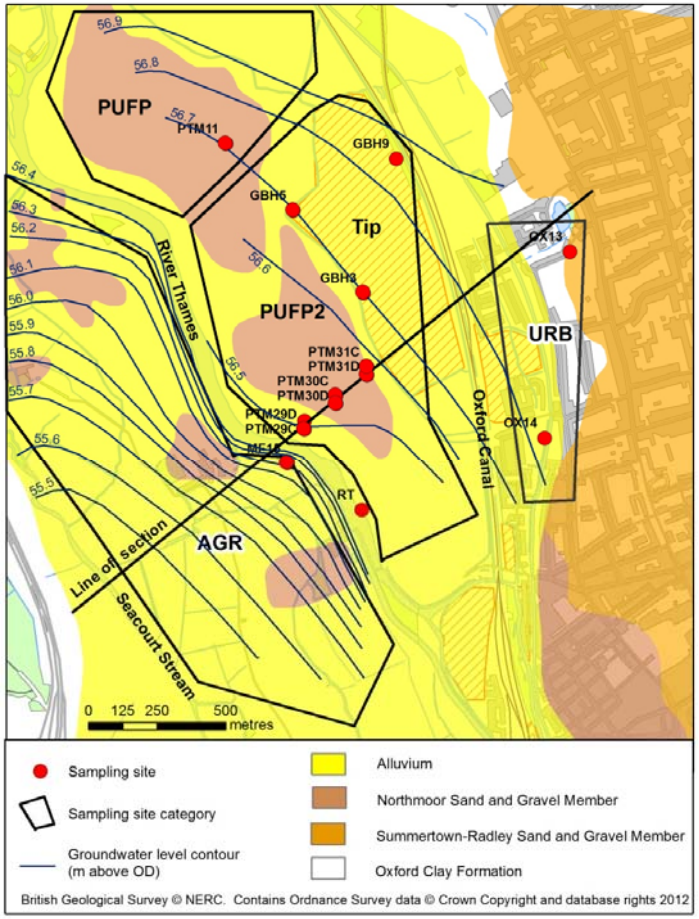
PFOS and PFOA

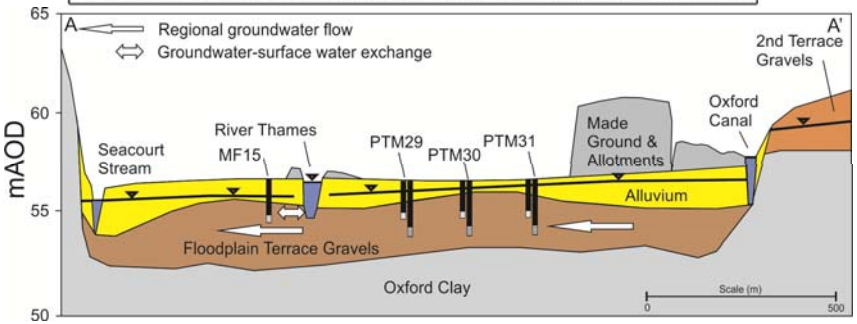
- Perfluoroalkane sulfonates and perfluoroalkanoic acids
- Many uses including fire-fighting foams and common household products
  - Widely detected in groundwater
  - PFOS very resistant to degradation

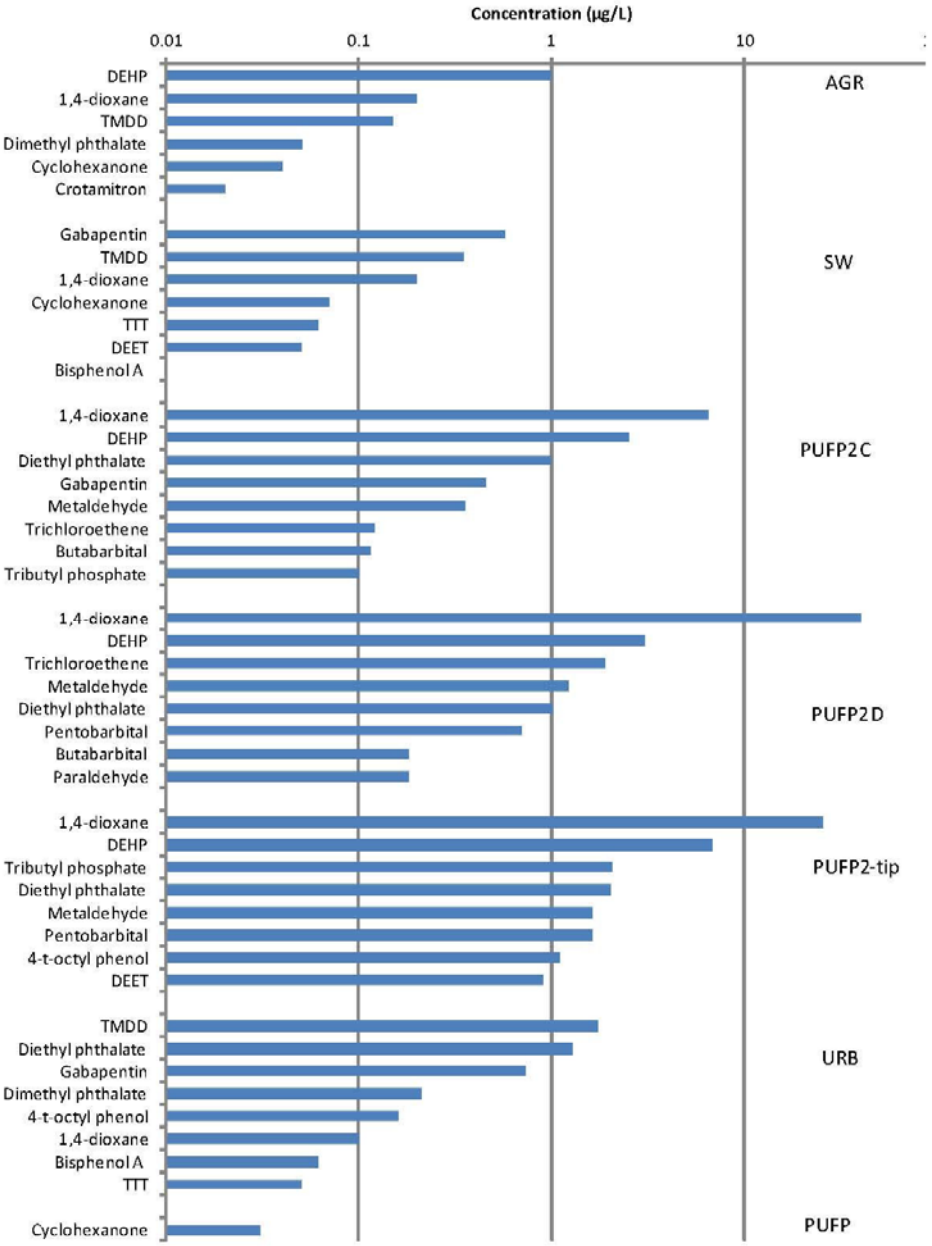
Robrock et al. (2006); Stapleton (2006); Environment Agency (2008)

Source fingerprinting

Port Meadow research site on Thames floodplain west of Oxford

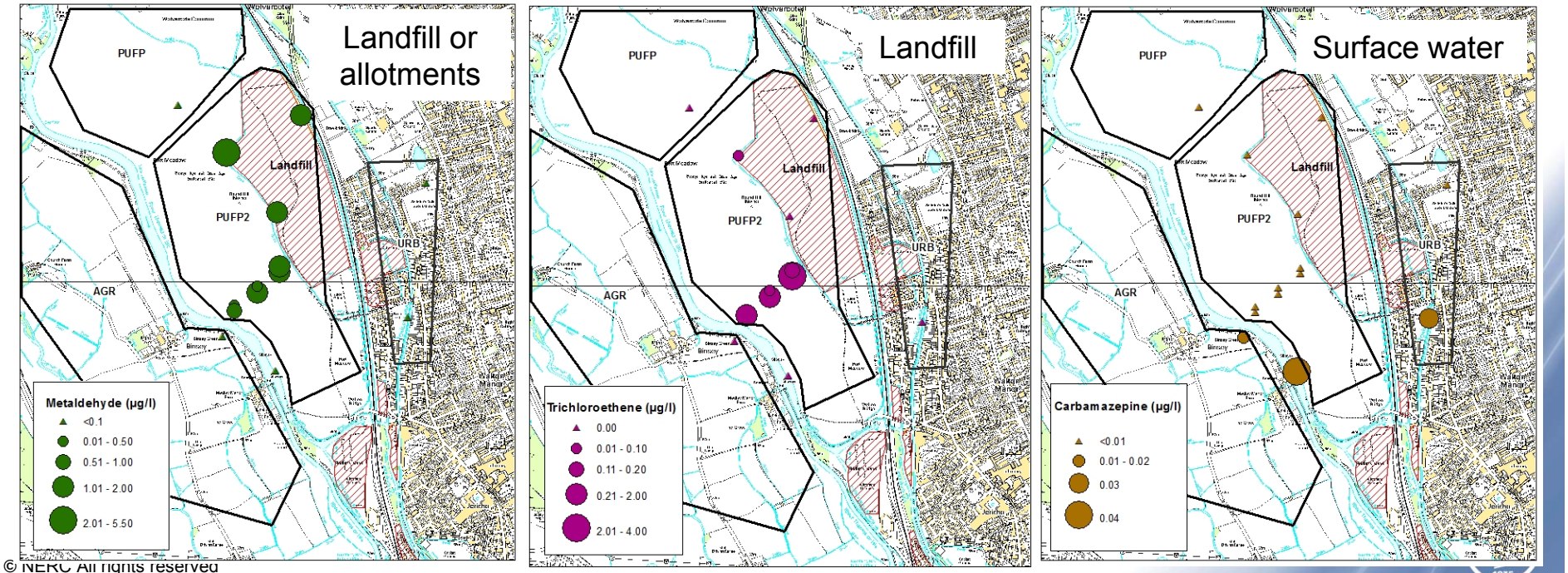




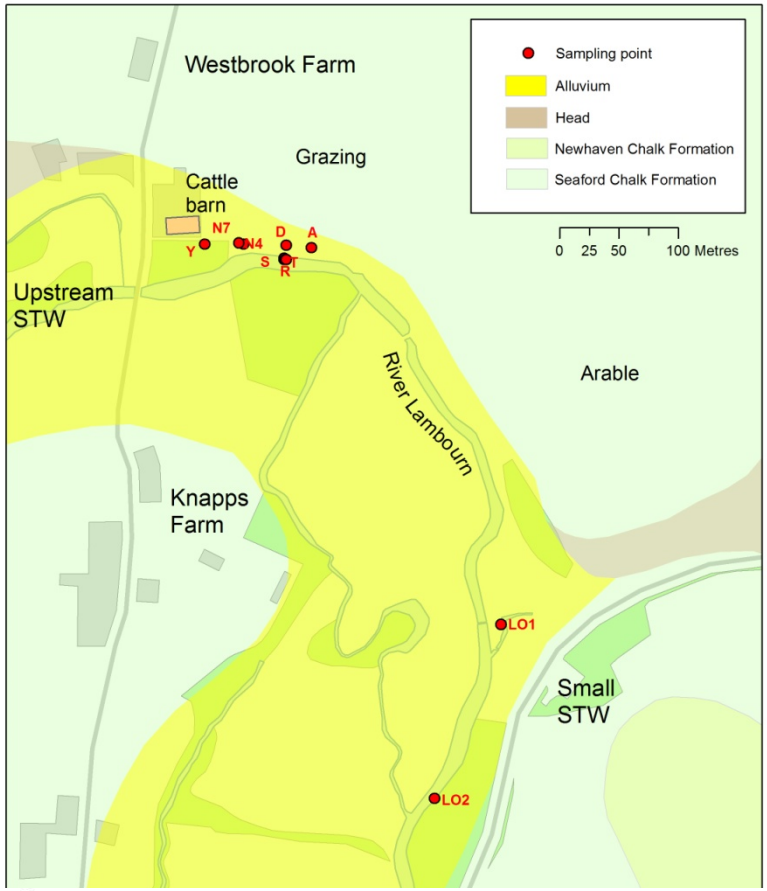


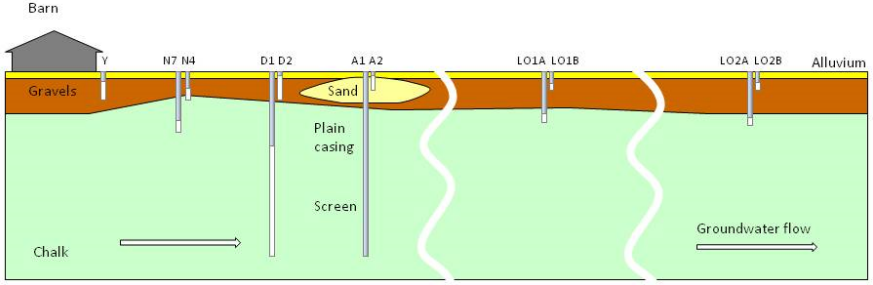
Port Meadow

- Microorganics fingerprint different types of water
- Largest source is landfill from both disposed and produced compounds
- Also input from surface water and urban area



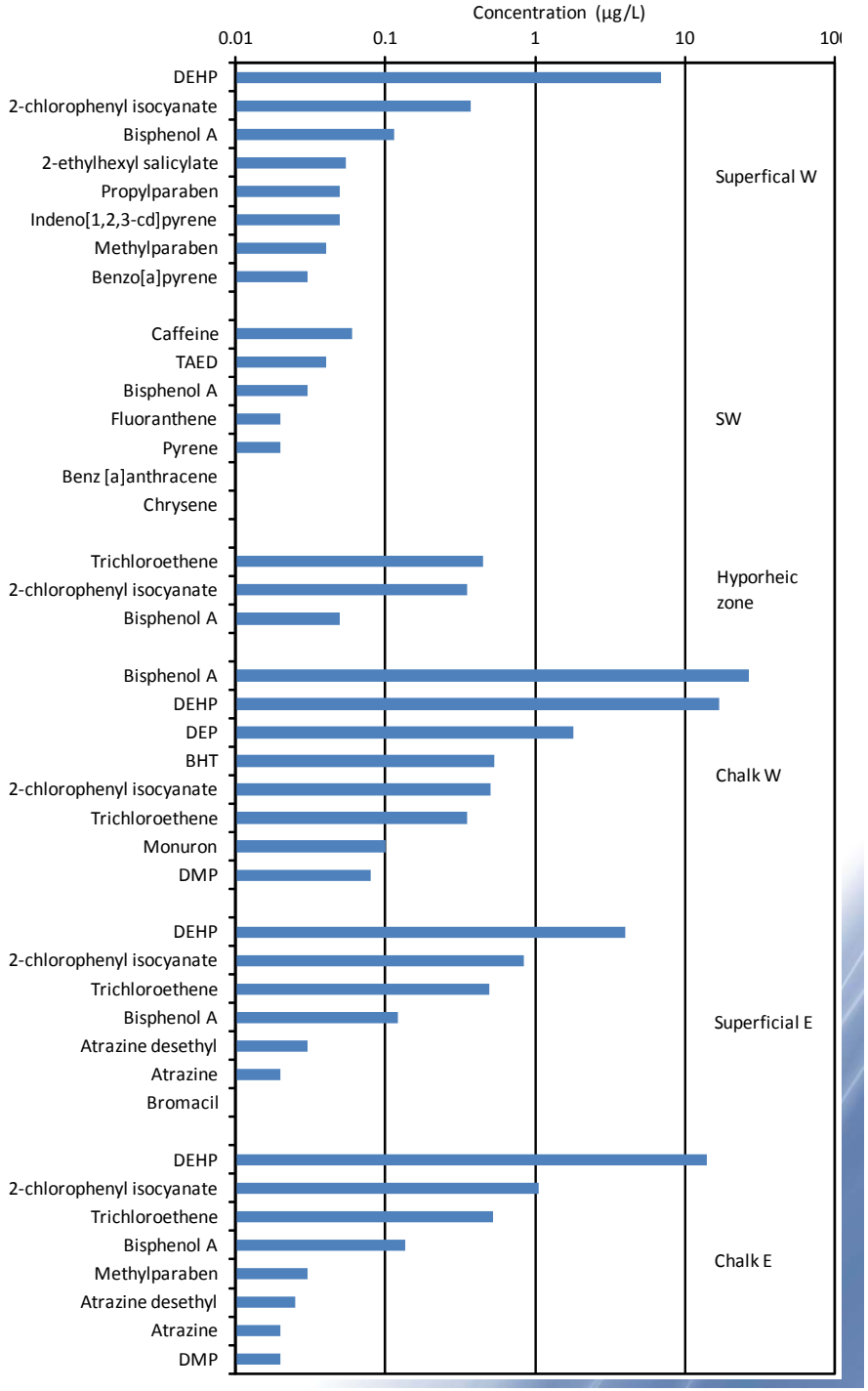
Source fingerprinting





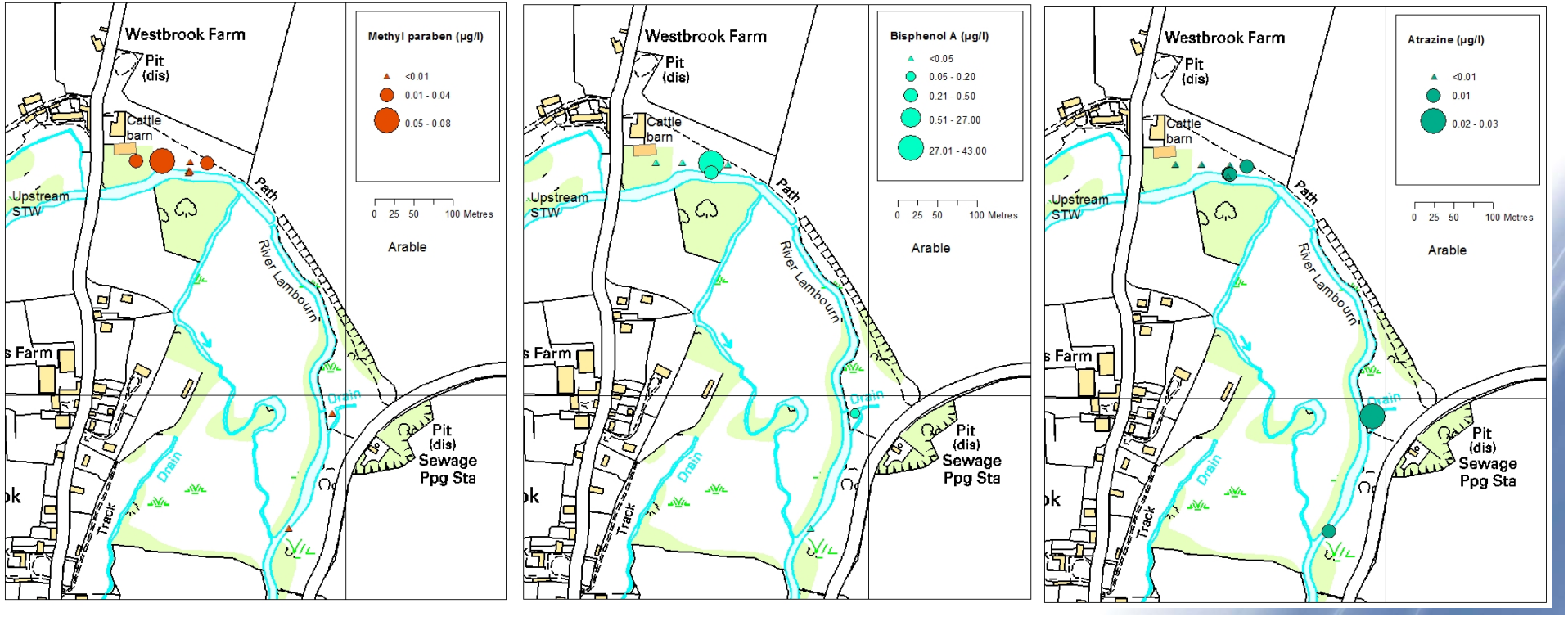
Boxford research site

Chalk downs



Boxford

- Sources from STW or cattle barn
- Also from agricultural area
- Hyporheic zone may be sink



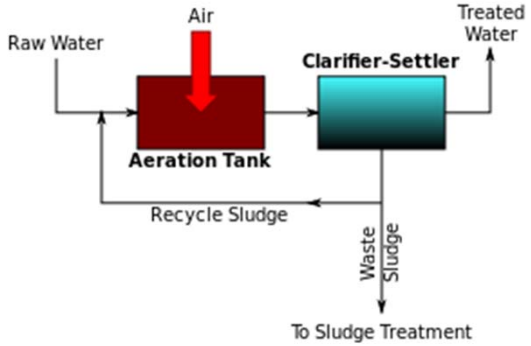
Risk assessment

- Need to take source-pathway receptor approach
- Source:
  - Usage
  - Formation in environment
- Pathway:
  - Define route
  - Persistence
  - Leachability
  - Water treatment recalcitrance, both waste and potable
- Impact on receptor:
  - Toxicity
  - Bioaccumulation potential
  - Synergistic effects
- Robust sensitive analytical method
  - Likely to include concentration step + GCMS or LCMS

Data

- Pesticides – have usage, solubility, K_{oc}, K_{ow}, DT_{50} and DW limit
- Pesticide metabolites - have some data on solubility, K_{oc}, K_{ow}, DT_{50}
  - Need metabolic pathway/rate and toxicity/bioaccumulation data
  - Some studies for UK
- Pharmaceuticals, personal care products and lifestyle compounds
  - Improving amounts data on aquatic persistence, particularly for pharmaceuticals, human and ecological effects at environmental levels
  - Studies on properties mainly addressing treatment recalcitrance
  - Prioritisation using PEC/PNEC principles plus sales/prescription data
  - Some ADIs available

Wastewater treatment



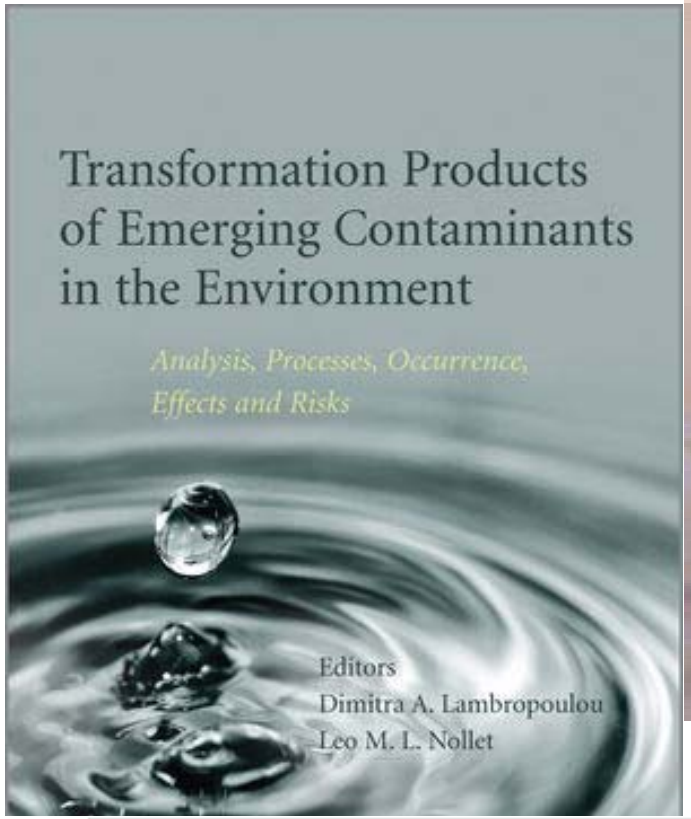
- Primary – settling and grease removal
- Secondary - fixed film or suspended growth (activated sludge) – many forms
- Tertiary – Filtration, nutrient removal, disinfection
- Inadequate retention time for EC elimination – 5 -10 days
- Polar compounds incompletely sorbed:
  - Parent e.g. β-blockers
  - Conjugates with gluconaric acid or sulphate
- Increased metabolites:
  - Musks
  - APEs
- Disinfection byproducts

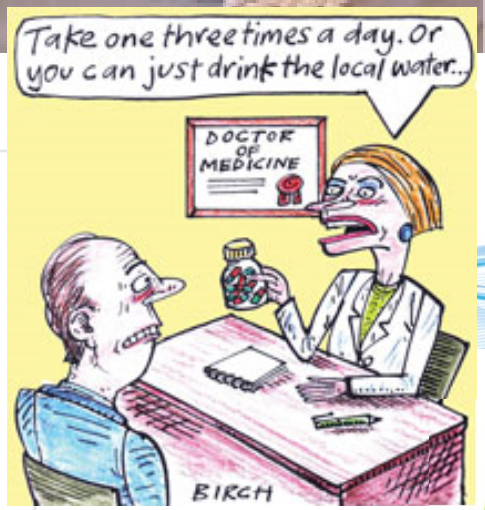
Drinking water treatment

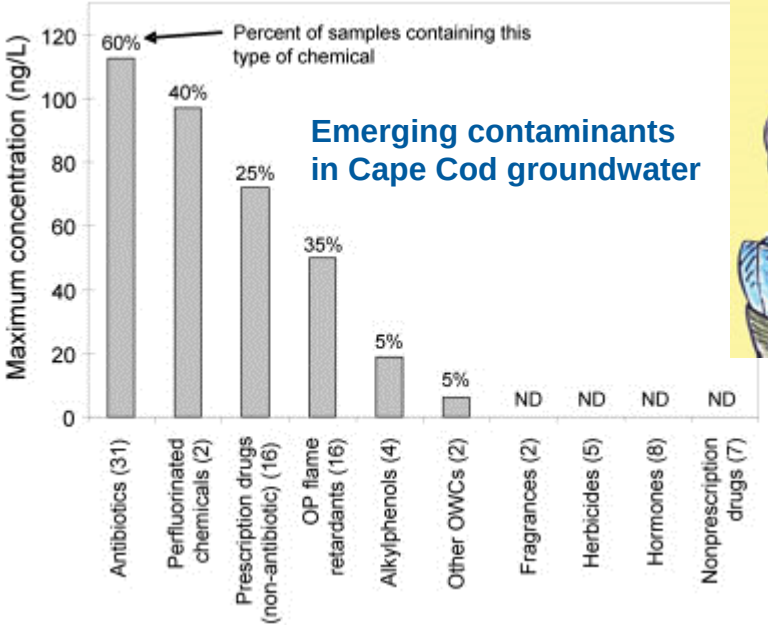
- Low percentage removed by clarification
- Many ECs not fully removed by combined or free chlorine and can produce undesirable by-products
- GAC or PAC filtration useful for compounds with K_{ow}>3
- Ozonation effective for compounds with double bonds, aromatic structure or heteroatoms such as N or S
- Also other advanced oxidation methods (AOP) e.g. using H_2O_2 or OH radical generated by UV, sensitised processes using semiconductors
- Membrane or nano filtration can be effective for negatively charged compounds

Conclusions

- Many different sources and pathways into groundwater: wastewater, biosolids from water treatment and animal wastes are important
- Frequently detected groups of ECs include antimicrobials, lifestyle compounds, pharmaceuticals
- Although mostly detected in low ng/L concentrations in groundwater there are many examples of hot spots
- TPs can be found at concentrations higher than the parent and may be more mobile or polar, and more toxic
- ECs can be typical of source/landuse
- Some are recalcitrant during water treatment
- Are starting to be regulated







Emerging contaminants in Cape Cod groundwater